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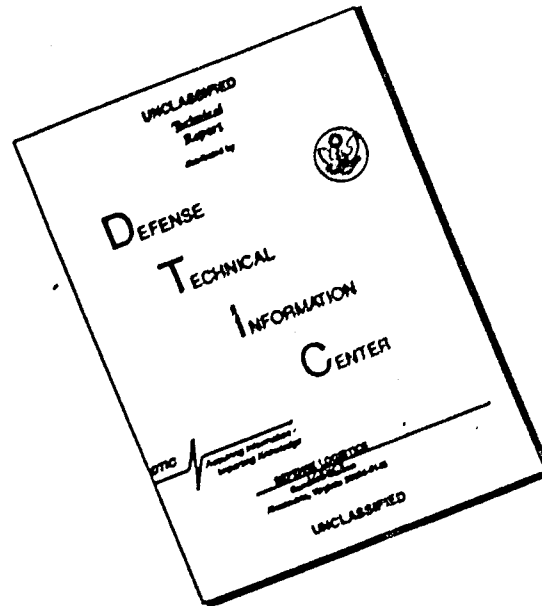
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LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA
DEPARTMENT OF PHYSICS
THE UNIVERSITY OF CHICAGO

LECTURES ON
SELECTED TOPICS IN THE THEORY OF
MOLECULAR ELECTRONIC STRUCTURE AND SPECTRA

ROBERT G. PARR

SPECIAL TECHNICAL REPORT

1957

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Special Topics in the Quantum Theory of
Molecular Electronic Structure

(A series of eight lectures given in June and
July, 1957, in the Department of Physics,
The University of Chicago, Chicago, Illinois)

Robert G. Parr
Professor of Chemistry
Carnegie Institute of Technology
Pittsburgh 13, Pennsylvania

PREFACE

In these lectures I will deal with what for short may be termed the quantum theory of valence -- the theory of the electronic structure of molecules in normal states, in excited states, and in course of reaction.

In these lectures I will try to deal frankly with this field as it is today -- a hodgepodge of good theories and bad, new theories and old, well-founded ideas and false notions -- a mixture of precise theorizing and crude empiricism -- a stamping ground for mathematical physicists and experimental chemists alike. (Concerning this last, just ask the fellow sitting next to you in this room what his background is!)

In these lectures I will deal in the main with work recently done at Carnegie Institute of Technology, but I also will try to develop a view of the overall picture.

I will give many references to the recent literature. I have not made an exhaustive literature search, however, and so I may have missed important papers.

§1. THE NATURE OF THE PROBLEM^{1,2}

We are interested in molecules in a course of reaction, yes, but right away let us restrict ourselves to the Schrödinger equation for the stationary state of a molecule:

$$\underline{H} \underline{\Psi} = E \underline{\Psi}. \quad (1.1)$$

This we do because before we can understand reactions we must understand molecules in isolation.

For a given molecule (that is, for a given \underline{H}) the problem of solving 1.1 is equivalent to the problem of finding well-behaved independent functions $\underline{\Psi}$ which minimize the expression

$$\bar{E} = \frac{\int \underline{\Psi}^* \underline{H} \underline{\Psi} d\tau}{\int \underline{\Psi}^* \underline{\Psi} d\tau}. \quad (1.2)$$

This variational theorem is fundamental; we quote it without proof.

In these equations \underline{H} is the quantum-mechanical Hamiltonian operator for the molecule (see below), E or \bar{E} is the energy of the molecule, and $\underline{\Psi}$ is the wave function for the molecule. When 1.1 is satisfied or 1.2 is minimized $\underline{\Psi}$ is an eigenfunction and E or \bar{E} is an eigenenergy for the molecule; these E are the ground and excited energies of the molecule known to the molecular spectroscopist.

Of course we are interested in many many properties of a molecule other than the energy. But as Boys has emphasized,³ getting the value of a property is trivially easy compared with obtaining an eigenfunction -- that is the fundamental problem with which we are faced.

The wave functions Ψ depend on both electronic and nuclear coordinates. Born and Oppenheimer have shown that due to the smallness of the ratio of the mass of an electron to the mass of any nucleus, however, to a good approximation one may proceed in a simplified way.⁴ To determine the total energy E for a given fixed configuration of the nuclei, one merely can add to the potential energy of nuclear repulsion,

$$V_{nn} = \frac{1}{2} \sum_{\alpha\beta} (Z_{\alpha} Z_{\beta} e^2 / r_{\alpha\beta}), \quad (1.3)$$

an electronic energy E_{el} determined by solution of an electronic Schrödinger equation,

$$\underline{H}_{el} \Psi_{el} = E_{el} \Psi_{el}, \quad (1.4)$$

or the corresponding variational equivalent; thus:

$$E = E_{el} + V_{nn}. \quad (1.5)$$

Here \underline{H}_{el} contains the kinetic energy of the electrons, their potential energy of attraction for the nuclei, and their potential energy of mutual repulsion:

$$\underline{H}_{el}(1,2,\dots,n) = \sum_{i=1}^n \underline{T}(\zeta_i) + \sum_{i=1}^n \sum_{\alpha} (Z_{\alpha} e^2 / r_{\alpha\zeta_i}) + \frac{1}{2} \sum_{i,j=1}^n (e^2 / r_{\zeta_i\zeta_j}). \quad (1.6)$$

The nuclear motions themselves can be taken care of by a later calculation in which E enters as a potential energy term; the total wave function thus is of the factorized form

$$\Psi = \Psi_{el} \Psi_{nucl} \quad (1.7)$$

where Ψ_{nucl} depends on nuclear coordinates alone. The functions Ψ_{el} can be determined for each nuclear configuration by solution of the variational equivalent of 1.4.

Our problem, in these terms, is to find, for given nuclear configurations (hence given V_{nn}), electronic wave functions Ψ_{el} which minimize the expression

$$\bar{E}_{el} = \int \Psi_{el}^* \underline{H}_{el} \Psi_{el} d\tau / \int \Psi_{el}^* \Psi_{el} d\tau. \quad (1.8)$$

Since \underline{H}_{el} can be written down at inspection for any molecule, the problem thus stated is a purely mathematical one.

Solution usually is carried out iteratively: one takes a Ψ in some assumed parametric form, as for example as a series of given starting functions with unknown coefficients, and one determines values of parameters (coefficients) which minimize the expression 1.8. If enough such variation is carried out, the exact wave function will be obtained. The basic problem of modern valence theory simply is the problem of developing the machinery for carrying out this procedure for molecules of interest: (a) to find suitable starting variation functions, (b) to evaluate basic integrals involving these starting functions, and (c) to carry out the minimization procedure itself. Of these three aspects of the problem, the first perhaps is the most subtle, the second certainly is the most difficult, and the third has been most alleviated by the availability of high-speed electronic computing equipment.

To indicate more concretely the nature of this problem, we may review briefly the situation as regards the simplest atoms, H and H-like atoms, and He.

For H or an H-like atom of nuclear charge Z , there is no problem (as you all know) -- exact solution is possible. How about He? This problem has been solved essentially exactly by Hylleraas and others,⁵⁻⁷ by using variation functions explicitly containing the interelectronic distance r_{12} . This seems at first very well and good, but there is one trouble: the method has not been found extensible to more complex systems.

What can we do? We can try to construct wave functions for He in some other way, that is extensible. For example, we may try to use one-electron functions. The most natural set is just the H-like set of orbitals, or more simply, the Slater orbitals,

$$(n,l,m)^S = (2Z)^{n+1/2} (2n!)^{-1} r^{n-1} \exp(-Zr) Y_{l,m}(\theta, \phi) \quad (1.9)$$

We abbreviate $(1s) \equiv (1,0,0)$, etc.

For the two-electron case of He we can forget about electron spin and try two-electron symmetrical products of one-electron functions. For example, we might simply take $\psi_{el} = 1s(1)1s(2) \equiv (1s)^2$. We then find the energy listed in Table I, with the best possible S off by 0.056 atomic units (a.u.). This is not good, for it is $0.056 \times 27 \times 23 \approx 35$ kcal per mole -- of the order of magnitude of energies of chemical interest. This is typical of the general situation and leads to the rather unpleasant conclusion that the problem of absolute predictions in chemical quantum mechanics is of the same level of difficulty as the problem of the absolute prediction of atomic spectroscopic intervals.

One can improve the situation with He considerably by mixing with the $(1s)^2$ function functions of the same or other types, as is shown in Table I.⁸ Modification of the form of the orbital itself leads to the so-called Hartree-Fock result, 0.042 au off. This leaves a residual error of ca. 0.5 ev per electron which is called the correlation energy. By going to an "open-shell" function, Eckart showed that a much better result still is obtained -- 0.028 au off. This function contains much of the radial correlation energy. Angular correlations were brought in by Taylor and Parr, as indicated in Table I, reducing the error still further to 0.006 au, which however still is 4 kcal/mole. More terms would of course ultimately remove the residual error.

This method of building up an exact wave function by linearly mixing more and more products of one-electron functions is called the method of configuration interaction. It will be fundamental in much of our later discussion.

TABLE I. Some variation functions for the normal helium atom.^a

Function ^{b,c}	E_{calc}	$E_{\text{calc}} - E_{\text{exptl}}$
$(1s)^2$	-2.848	0.056
$(ns)^2$ with $n=0.955$	-2.854	0.050
$(\phi)^2$	-2.861	0.042
$(1s)(1s')$	-2.876	0.028
$(1s1s')+(2p)^2$	-2.895	0.008
$(1s1s')+(2p)^2+(3d)^2$	-2.897	0.006
$(1s1s')+(2p)^2+(3d)^2+(4f)^2$	-2.897	0.006
Exact	-2.903	0

a. Energies in atomic units: $e^2/a_0 = 27.2$ ev.

b. See references 6, 8 and 17. The second function is due to Parr and Joy, the third function is the Hartree-Fock function, the fourth function is due to Eckart, the fifth, sixth and seventh functions are due to Taylor and Parr, and the last (exact) function is due to Hylleraas and later authors, the most accurate calculation of all being that of Kinoshita.

c. The sign + in a function stands for "mixed linearly with".

§2. A CENTRAL ORBITAL TREATMENT OF THE HYDROGEN MOLECULE

We thus see what we are up against in the general case.

The hydrogen molecule-ion we certainly expect to be favorable -- it has but one electron! Indeed this problem has been solved exactly. There seems little possibility of use of the rather complicated wave functions thus obtained for larger problems, however, although Wallis and Hulburt recently have made a start.⁹

The hydrogen molecule is more interesting. In their well-known beautiful but very tedious calculation, James and Coolidge solved this problem essentially exactly, using a variational method patterned after the one used by Hylleraas for helium. But again extensibility is lacking.

Some sort of orbital approach seems most desirable. You are all familiar with several calculations using atomic orbitals centered on the two nuclei; some of the results are exhibited in Table II.¹⁰ While the results are satisfactory to a degree, it will be noted from the table that nobody has come within 0.017 au or 11 kcal/mole of the correct energy using atomic orbitals.

The 0.017 au discrepancy can in principle be removed by adding (mixing) more terms built from conventional orbitals, and it certainly will be one of these days. The main reason it hasn't yet resides in the integrals problem.

This, plus other factors, motivated Mr. Joy and I to try the use of a set of orbitals simpler to deal with, orbitals centered at the molecular center only!¹¹⁻¹⁸ Results are shown in Table II; they are, I think, quite encouraging.

We found it expedient and workable to remove the restriction that the principal quantum number n be integral. It is only necessary to regard the quantity $(2n)!$ of 1.9 as the factorial or gamma function, and to be prepared for evaluation of complete and incomplete gamma and beta functions of non-integral argument. A corresponding somewhat startling result for the helium atom is given in Table I -- it is found that the best $(ns)^2$ description for helium has $n=0.955$, which means that the best single ns orbital for helium is infinite at the nucleus!

These calculations have been performed on an IBM 650. Subroutines for evaluating the required auxiliary functions have been developed and packed into a single master subroutine, and another subroutine has been written for variational determination of an energy minimum in many dimensions by the method of steepest descents. An alternative to the last, fitting of many-dimensional parabolas to the energy function, has also been studied in some detail. It may be noted that in the last "central orbital" function listed in Table II there are 22 independent variational parameters; all these actually are varied in this calculation.

These calculations are still in progress; I see no reason why they should not be extended to give any desired accuracy.

It may be instructive to look at a typical formula for these calculations. The energy associated with a single $(ns)^2$ term in hydrogen or helium is given by the following expression:¹⁷

$$\bar{E} = T + V_{ne} + V_{ee} + V_{nn} . \quad (2.1)$$

TABLE II. Some variation functions for the normal hydrogen molecule.^a

Function ^{b,c}	E_{calc}	$E_{\text{calc}} - E_{\text{exptl}}$
Heitler-London (variable Z)	-1.138	0.036
LCAO MO (variable Z)	-1.128	0.046
Weinbaum (variable Z)	-1.147	0.027
Hartree-Fock	-1.132	0.042
Callen-James (best function without r_{12})	-1.157	0.017

$(1s)^2$	-0.988	0.186
$(ns)^2$ with $n=1.25$	-1.026	0.148
$(ns)(n's') = (ss')$	-1.034	0.140
Best central orbital function from s orbitals	-1.045	0.129
$(ss') + (sd_0)$	-1.112	0.062
$(ss' + (s''d_0) + (p_0p_0')$	-1.128	0.046
$(ss') + (s''d_0) + (p_0p_0' + (p_1p_{-1})$	-1.139	0.035
$(ss') + (s''d_0) + (p_0p_0' + (p_1p_{-1}) + (s''g_0)$	-1.149 ^d	0.025
Exact	-1.174	0

a. Energies in atomic units: $e^2/a_0 = 27.2$ ev. All calculations are for the observed internuclear distance, $R = 1.4 a_0$.

b. See references 10,12, 17 and 18. The central orbital functions (listed below the dotted line) are all due to Joy and Parr except the fourth, which is due to Shull and Hagstrom. The "exact" function is due to James and Coolidge, the agreement with experiment being perfect for it to the number of significant figures listed.

c. The sign + in a function means "mixed linearly with".

d. By adding further terms, Joy has obtained -1.159 au.

Here (in e^2/a_0 units)

$$T = \zeta^2 / (2n-1), \quad (2.2)$$

$$V_{ne} = -4(\zeta/n) [1 - I(2n-1, \zeta) + (2n/\zeta) I(2n, \zeta)], \quad (2.3)$$

$$V_{ee} = 2(\zeta/n) \frac{I_1(2n+1, 2n)}{2}, \quad (2.4)$$

$$V_{nn} = (\zeta/\varrho) \text{ for } H_2, 0 \text{ for He}, \quad (2.5)$$

where $\varrho = \zeta R$, $I(x, \zeta)$ is the ratio of the incomplete gamma function to the corresponding complete gamma function, and $I_x(a, b)$ is the ratio of the incomplete beta function to the corresponding complete beta function.

Reduction of 2.1 to the familiar $(1s)^2$ result for helium goes as follows. Let $n=1$, $\varrho=0$. Then $T = \zeta^2$, $V_{ne} = -4\zeta$, $V_{nn} = 0$, and

$$V_{ee} = 2\zeta \frac{I_1(3, 2)}{2} = 2\zeta \frac{\int_0^1 t^2(1-t)dt}{\int_0^1 t^2(1-t)dt} = (5/8)\zeta.$$

Thus

$$\bar{E} = \zeta^2 - 4\zeta + (5/8)\zeta = \zeta^2 - (27/8)\zeta.$$

This is the familiar result; \bar{E} has its minimum value, $-(27/16)^2$ or -2.848 au, when $\zeta = 1.6875$.

§3. THE GENERALIZED HUCKEL METHOD: PREFACE²

I wish to describe in this and the next several sections a theory that recently has been developed for calculating from quantum mechanics some of the properties of certain types of complex molecules. As you will see, the theory is far from perfect. But it represents I think a fairly good example of the sort of thing one should want and be able to do better in the future.

We are going to have to deal with the quantum mechanics of many-electron systems; in this section I shall quickly survey some mathematics necessary for the discussion and also set the scene historically.

The linear variational method

It is well-known that if one takes as a variational function for a given molecule a linear combination of a given set of known starting functions,

$$\Psi = A_1 f_1 + A_2 f_2 + \dots + A_p f_p, \quad (3.1)$$

then the best such function, the one that makes the energy of 1.2 a minimum,

has coefficients A_i which satisfy the equations

$$\sum_{i=1}^P A_i (H_{ij} - S_{ij} \bar{E}) = 0, \quad j = 1, 2, \dots, P; \quad (3.2)$$

and further that the corresponding best energy is a solution of the secular equation

$$\left| (H_{ij} - S_{ij} \bar{E}) \right| = 0, \quad (3.3)$$

where the matrix elements H_{ij} and S_{ij} are the numbers

$$H_{ij} = \int f_i^* \underline{H} f_j d\tau, \quad S_{ij} = \int f_i^* f_j d\tau. \quad (3.4)$$

The whole story of resonance, in a sense (My apologies to Professor Wheland!), resides in these equations -- Here the f 's represent the various "contributing structures", Ψ represents the actual molecule, and the "resonance energy" is the energy increment $H_{11} - \bar{E}_1$, where H_{11} is the smallest of the H_{ij} and \bar{E}_1 is the lowest root of 3.3.

The secular equation 3.3 has p roots; these approximate the ground and excited-state energies of the given molecule.

Determinantal wave functions

We will not be able to escape explicit consideration of electron spin if we wish to be at all precise in our descriptions of many-electron systems -- you all know that we must impose the Pauli exclusion principle on all of our wave functions. That is, all wave functions must be made antisymmetrical with respect to exchange of any two electrons. Or equivalently, if one is building n -electron wave functions linearly from products of one-electron wave functions (orbitals) and spin functions α and β , one may restrict oneself to consideration of antisymmetrized products of the type

$$\begin{aligned} & \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\beta(1) & \dots \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_2(2)\beta(2) & \dots \\ . & . & . & . & . & . & . \end{vmatrix} \\ &= \frac{1}{\sqrt{n!}} \sum_P (-1)^P P [\phi_1(1)\alpha(1) \phi_1(2)\beta(2) \phi_2(3)\beta(3) \dots] \\ &= (\phi_1 \bar{\phi}_1 \bar{\phi}_2 \dots) = \bar{\Psi}. \end{aligned} \quad (3.5)$$

Here a number of equivalent notations have been introduced for one and the same thing, a determinant times a factor which makes the resultant function normalized if the ϕ , and α and β , are orthonormal. Even more concisely, if the symbol λ is used to represent the product of some ϕ with α or β , a spinorbital, then the typical function to be dealt with may be written

$$(\lambda_1 \lambda_2 \lambda_3 \dots)$$

In this last notation, note that no two λ 's can be the same (or else the function would be identically zero); the () may be thought of as a notation for "take the antisymmetrized product of the functions".

To give a simple example, the ground state wave function for the hydrogen molecule, including spin, in the Heitler-London, molecular orbital and Weinbaum forms may be written as follows (omitting normalizing factors):

$$\begin{aligned}\Psi_{\text{H.L.}} &= (\chi_a \bar{\chi}_b) + (\chi_b \bar{\chi}_a), \\ \Psi_{\text{M.O.}} &= (\phi_1 \bar{\phi}_1) = (\chi_a \bar{\chi}_b) + (\chi_b \bar{\chi}_a) + (\chi_a \bar{\chi}_a) + (\chi_b \bar{\chi}_b) \\ \Psi_{\text{WEINBAUM}} &= A [(\chi_a \bar{\chi}_b) + (\chi_b \bar{\chi}_a)] + B [(\chi_a \bar{\chi}_a) + (\chi_b \bar{\chi}_b)] \\ &= C (\phi_1 \bar{\phi}_1) + D (\phi_2 \bar{\phi}_2)\end{aligned}\tag{3.6}$$

Here χ_a and χ_b are atomic orbitals on atoms A and B, and ϕ_1 and ϕ_2 are the corresponding LCAO combinations $\chi_a + \chi_b$ and $\chi_a - \chi_b$, respectively.

The last of equations 3.6 illustrates a very important point. If one starts from a given set of atomic orbitals the Heitler-London method including ionic terms and the molecular orbital method including configuration interaction both give the same final wave function. In their primitive forms the methods however are of course different.

The pi-electron approximation

The molecules we shall be dealing with are in the main the large unsaturated, usually planar, often conjugated organic molecules such as ethylene, benzene, polyenes, and dyes. There is a great literature on the conjugation in these molecules, most of which makes at least qualitative use of what we shall call the pi-electron approximation - the assumption that the electrons in the so-called pi bonds of these molecules move around quite freely and quite independently of the details of what may be happening in the underlying sigma-bonded structures. We may think of a core in the field of which the pi electrons move, if you like. Quantum-mechanically, we may hope to treat the aromatic properties of benzene, for example, as a six-electron problem.

How this approximation is invoked in the various theories we shall see immediately. Then later we shall submit it to a rather detailed re-examination -- it is really the "core" of the matter!

The Hückel method

In the Hückel method for treating these molecules, a very nice simplified system is used for calculating a variety of properties. The method may be characterized as having four defining assumptions, as follows:

Assumption 1: The pi electrons are treated apart from the rest. That is, "the pi-electron approximation is invoked".

Assumption 2: The pi-electron wave functions are built from $2p\pi$ atomic orbitals χ_p on the various atoms. These orbitals are combined linearly to give molecular orbitals ϕ_i :

$$\phi_i = \sum_p C_{ip} \chi_p.\tag{3.7}$$

The coefficients C_{ip} are determined so as to minimize the total pi-electron energy. Wave functions for the complete pi-electron system are formed by assigning one or two electron at most to the molecular orbitals ϕ_i .

Assumption 3. For the energy calculation it is assumed that the several pi electrons move independently in a potential field described by a one-electron Hamiltonian operator; thus the total pi-electron Hamiltonian operator is taken to have the form

$$\underline{H}_{\pi}(1,2,\dots,n_{\pi}) = \sum_{i=1}^{n_{\pi}} \underline{H}_{\text{eff}}(\mu), \quad (3.8)$$

where mutual pi-electron repulsions are assumed taken care of in the operator $\underline{H}_{\text{eff}}$.

Assumption 4. The basic coulomb integrals

$$\alpha_p(\text{eff}) = \int \chi_p(1) \underline{H}_{\text{eff}}(1) \chi_p(1) d\tau(1) \quad (3.9)$$

and resonance integrals

$$\beta_{pq}(\text{eff}) = \int \chi_p(1) \underline{H}_{\text{eff}}(1) \chi_q(1) d\tau(1), \quad p \neq q, \quad (3.10)$$

are taken to be empirical properties of atoms and bonds, respectively, and the overlap integrals

$$S_{pq} = \int \chi_p(1) \chi_q(1) d\tau(1), \quad p \neq q, \quad (3.11)$$

are computed theoretically or set equal to zero.

The consequences of these assumptions are that electron spin can be almost forgotten and the total pi-electron wave functions taken as simple products of molecular orbitals ϕ_i , with the coefficients C_{ip} determined upon solution of a one-electron secular equation of the form

$$\begin{vmatrix} \alpha_a - e & \beta_{ab} - S_{ab}e & \dots \\ \beta_{ba} - S_{ba}e & \alpha_b - e & \dots \\ \vdots & \vdots & \ddots \end{vmatrix} = 0. \quad (3.12)$$

Further, the total pi-electron energy is a simple sum of the appropriate roots of this equation:

$$E_{\pi} = \sum_i e_i. \quad (\text{sum over filled orbitals}) \quad (3.13)$$

This method has been developed and extensively applied by Coulson and Longuet-Higgins, Mulliken, and many others. Its great advantage is its simplicity. It fails when used for spectra, however, and doesn't look too good when looked at from the fundamental point of view. (The most basic trouble, as we shall see, is with Assumption 3.)

The Goeppert-Mayer and Sklar method

In a famous 1938 paper,¹⁹ Goeppert-Mayer and Sklar inaugurated calculations by a method seemingly so different from the Hückel method that the two methods had nothing in common. Characteristics of this method in its most refined form are as follows:

Assumption 1: The pi electrons are treated apart from the rest.

Assumption 2: The pi-electron wave functions are built from $2p\pi$ atomic orbitals χ_p on the various atoms. These orbitals are combined linearly to give molecular orbitals ϕ_i as in 3.7. Various many-electron functions are built up as antisymmetrized products Φ_k of appropriate ϕ_i and spin factors, as in 3.5. If one wishes to employ a single such Φ as the description of a molecular state, one can determine the values of the coefficients C_{ip} by minimization of the total energy (Roothaan's LCAO SCF procedure²⁰); if one wishes to mix many such Φ linearly (the configuration interaction or CI procedure²¹), the values of the C_{ip} are immaterial.

Assumption 3. The pi-electron Hamiltonian operator is taken to have the form

$$\underline{H}_\pi(1,2,\dots,n_\pi) = \sum_{\mu=1}^{n_\pi} \underline{H}_{\text{core}}(\mu) + \frac{1}{2} \sum_{\mu,\nu=1}^{n_\pi} (e^2/r_{\mu\nu}). \quad (3.14)$$

Pi-electron repulsions thus are explicitly considered; reasonable approximations are invoked to elucidate $\underline{H}_{\text{core}}$.

Assumption 4. All integrals are computed theoretically. These are of four types, the one-center core integrals

$$\alpha_p(\text{core}) \equiv \alpha_p = \int \chi_p(1) \underline{H}_{\text{core}}(1) \chi_p(1) dv(1), \quad (3.15)$$

the two-center core integrals

$$\beta_{pq}(\text{core}) \equiv \beta_{pq} = \int \chi_p(1) \underline{H}_{\text{core}}(1) \chi_q(1) dv(1), \quad p \neq q, \quad (3.16)$$

overlap integrals as in 3.11, and electronic repulsion integrals

$$(pq|rs) = \iint \chi_p(1) \chi_q(1) (e^2/r_{12}) \chi_r(2) \chi_s(2) dv(1) dv(2). \quad (3.17)$$

Reasonable approximations are made to delineate the operator $\underline{H}_{\text{core}}$.

The difficulties of calculations by this scheme are literally horrendous (as many of you, and I well know!); the integrals are hard to compute and there are many of them ($n^4/8$ of the type 3.17 for a large molecule with no symmetry!). But the method does give pretty fair agreement with spectra and certainly seems more satisfactory from the fundamental point of view.

The method of atoms in molecules of Moffitt

A few words now must be said about the so-called method of atoms in molecules.²² We shall come back to this latter. Suffice it here to say that

after finding disappointing results by the Goeppert-Mayer and Sklar method for the oxygen molecule,²³ Moffitt decided that in molecular calculations one should correct for the inadequacies of the orbital approximations by making use of available spectroscopic data for atoms. He obtained some good results this way for oxygen, and he gave an elaborate general prescription for calculation.

Requirements of a useful theory of complex unsaturated molecules

With what has been said in mind, it is not hard to set down a number of characteristics that would be desirable in a theory of the electronic structure of molecules of the order of complexity of benzene, pyridine, naphthalene and such molecules. I get six:

- (1) Pi electrons should be treated apart from the rest.
- (2) Pi-electron wave functions should be built from $2p\pi$ atomic orbitals.
- (3) Pi-electron repulsions should be included.
- (4) The treatment of pi-electron repulsions should be simplified.
- (5) Provision for the use of atomic spectroscopic data should be made.
- (6) Empirical elements should be included.

More strictly we should of course admit that what we are talking about is not a theory but a method. Requirements 1 and 4 are necessary to make the method manageable; requirement 2 is an expression of our conviction that our elementary ideas about orbitals in molecules are valid; requirement 3 is an absolute necessity if we are going to treat spectra (How else can we separate singlet and triplet states?), requirement 5 will allow us to get ionic and covalent states correctly located on the energy scale relative to one another, and requirement 6 will take care of the core and the errors forced on us by all of our other requirements.

§4. THE GENERALIZED HÜCKEL METHOD: OUTLINE

Basic assumptions

What method can we construct having the above properties? Dr. Rudolph Pariser of the duPont Company and I gave one in 1953 which has the following defining characteristics:^{24,25,28}

Assumption 1: Same as Assumption 1 of Goeppert-Mayer and Sklar method.

Assumption 2: Same as Assumption 2 of Goeppert-Mayer and Sklar method.

Assumption 3: Same as Assumption 3 of Goeppert-Mayer and Sklar method.

Assumption 4: The four types of integral that enter are determined in the following ways:

(a) The one-center core integrals of 3.15 are referred by a reasonable elucidation of the operator H_{core} to atomic ionization potentials, and the latter are taken from experiment.

(b) The two-center core integrals of 3.16 are taken to be empirical properties of bonds, (usually) set equal to zero for non-bonded atom pairs.

(c) The overlap integrals of 3.11 are set equal to zero.

(d) The electronic repulsion integrals of 3.17 all are set equal to zero save those n of the form $(pp|pp) \equiv \gamma_{pp}$ and those $n^2/2$ of the form $(pp|qq) \equiv \gamma_{pq}$. The first type, the one-center coulomb repulsion integrals, are obtained from relations of the form

$$\gamma_{pp} \equiv (pp|pp) = I_p - A_p, \quad (4.1)$$

where I_p and A_p are the ionization potential and electron affinity of atom p in its appropriate valence state, taken from experiment. The second type, the two-center coulomb repulsion integrals, γ_{pq} , are computed theoretically, estimated using charged-sphere or other pseudo-classical approximations, or determined empirically.

Elucidation of the basic assumptions

We need not dwell on Assumptions 1, 2 and 3. We are committing ourselves, you see, to the theoretical framework of the Goeppert-Mayer and Sklar method, which fundamentally has much more appeal than the framework of the Huckel method.

Assumption 4 has far-reaching consequences, and should be examined very carefully for their real meaning. We shall in our later critique of the method attempt to deal more severely with the fine points; for the time being a few supplementary remarks will have to do.

Concerning Assumption 4a, the elucidation used is that due to Goeppert-Mayer and Sklar. This gives the formula

$$\alpha_p = -I_p - \sum_{q \neq p} \gamma_{pq} - P_p, \quad (4.2)$$

where P_p is the total (positive) energy of attraction between a pi electron on atom p and the rest of the molecule, treated as neutral -- the total so-called penetration correction for α_p .

The physical meaning of the various terms in 4.2 is clear. α_p itself is the energy of an electron in atomic orbital χ_p in the core. $-I_p$ is the value of this energy in the isolated atom (assuming χ_p is an atomic eigenfunction), $-P_p$ is an additional stabilization due to the presence of the rest of the molecule when unstripped of its pi electrons, and the sum of repulsion integrals is the further stabilization obtained when pi electrons are stripped off the rest of the molecule.

Concerning Assumption 4b, this may be thought of as the place we have chosen most explicitly to acknowledge our ignorance of the precise structure of the molecular core and our realization that the quantum-mechanical calculation we are carrying out is by no means exact. This we shall return to later.

Concerning Assumption 4c, this should not be taken literally. Just as in the Huckel method the neglect of overlap can be shown to be a simplifying formal assumption that gives results essentially equivalent to results obtainable

without the assumption, so in the generalized method one is not saying "the overlap integrals are zero" but that "the overlap integrals may be set equal to zero". More also will be said about this later.

Concerning Assumption 4d, again the simplifications are to be regarded as formal, not interpreted literally. We may call the simplification,

$$(pq|rs) = 0 \text{ unless } \chi_p = \chi_q \text{ and } \chi_r = \chi_s, \quad (4.3)$$

the formal neglect of differential overlap. It has been shown to give results essentially the same as results obtained without it.^{24,26} This was its first justification, but more can be said and will be said later.

Concerning the evaluation of the one-center repulsion integrals by 4.1, this formula can be given a simple derivation using "atoms-in-molecules" ideas.²⁷ Suppose that using the pi-electron approximation we wanted to calculate the energy change for the atomic process $C + C \rightarrow C^+ + C^-$, where the electron transfer involves a pi electron. We would get, at inspection, the result

$$\Delta E(\text{calc}) = (pp|pp). \quad (4.4)$$

But this energy change can be obtained also from atomic data:

$$\Delta E(\text{exptl}) = I_p - A_p. \quad (4.5)$$

The rub is that these equations do not give the same result! Using 4.4 one finds $\Delta E = 17$ ev (for Slater orbitals); using 4.5 one finds $\Delta E = 11$ ev. This is of course because the theoretical calculation is wrong. What can we do? One thing would be to go to a better, more detailed theory. This we want to avoid, for simplicity. So we use an alternative, use the relation $(pp|pp) = I_p - A_p$ to give integrals $(pp|pp)$, with the hope that this will put things right.

Concerning the evaluation of the two-center repulsion integrals, it must be admitted frankly that this is a subtle problem. Methods various authors have used will be indicated as we go along; I will later give what I consider the best method of all (which has not yet been tried by anyone!).

A word of caution. The validity of 4.1 as a method of bringing in atomic data depends on the assumption of zero differential overlap's having been made.²⁹ Quite a different theory is obtained if one uses 4.1 without zero differential overlap.³⁰

§5. THE GENERALIZED HÜCKEL METHOD: APPLICATIONS TO ELECTRONIC SPECTRA

Before I begin cataloguing applications, which is not my main purpose anyway, I had better take up in some detail a simple example, ethylene, and then the most important example of all, benzene. I will then describe the applications that we ourselves have made to spectra, and those made by others.

Ethylene^{24,29}

The following scheme of equations shows the pi-electron Hamiltonian operator for this two pi-electron problem; construction of molecular orbitals ϕ_i as linear combinations of atomic $2p\pi$ orbitals χ_p ; formation of anti-symmetrized products Φ_j ; linear combination of the Φ_j to give approximations to the ground state N, the first excited singlet state V and the first excited triplet state T of the molecule; computation of the appropriate matrix elements by the standard Slater-Condon rules in terms of integrals over molecular orbitals; reduction of the integrals over molecular orbitals to integrals over atomic orbitals; and the final secular equation for the problem.

$$H_{\pi}(1,2) = H_{\text{core}}(1) + H_{\text{core}}(2) + (e^2/r_{12}). \quad (5.1)$$

$$\phi_1 = \frac{1}{\sqrt{2}} (\chi_a + \chi_b), \quad (5.2)$$

$$\phi_2 = \frac{1}{\sqrt{2}} (\chi_a - \chi_b).$$

$$\Phi_1 = (\phi_1\bar{\phi}_1), \quad \Phi_2 = (\phi_2\bar{\phi}_2), \quad \Phi_V = \frac{1}{\sqrt{2}} [(\phi_1\bar{\phi}_2) + (\phi_2\bar{\phi}_1)],$$

$$\Phi_T = \frac{1}{\sqrt{2}} [(\phi_1\bar{\phi}_2) - (\phi_2\bar{\phi}_1)] \quad (\text{one component}). \quad (5.3)$$

$$\Psi = A_1 \Phi_1 + A_2 \Phi_2 + A_V \Phi_V + A_T \Phi_T. \quad (5.4)$$

$$E_1 = H_{11} = 2I_1 + J_{11}, \quad E_V = H_{VV} = I_1 + I_2 + J_{12} + K_{12}$$

$$E_2 = H_{22} = 2I_2 + J_{22}, \quad E_T = H_{TT} = I_1 + I_2 + J_{12} - K_{12}$$

$$H_{1V} = H_{2V} = H_{1T} = H_{2T} = H_{VT} = 0,$$

$$H_{12} = K_{12}. \quad (5.5)$$

$$I_i = \int \phi_i(1) H_{\text{core}}(1) \phi_i(1) dv(1), \quad (5.6)$$

$$J_{ij} = \iint \phi_i(1) \phi_i(1) \left(\frac{e^2}{r_{12}} \right) \phi_j(2) \phi_j(2) dv(1) dv(2), \quad (5.7)$$

$$K_{ij} = \iint \phi_i(1) \phi_j(1) \left(\frac{e^2}{r_{12}} \right) \phi_j(2) \phi_i(2) dv(1) dv(2), \quad (5.8)$$

$$I_1 = \frac{1}{2} (\alpha_a + \alpha_b) + \beta_{ab} = \alpha + \beta,$$

$$I_2 = \frac{1}{2} (\alpha_a + \alpha_b) - \beta_{ab} = \alpha - \beta, \quad (5.9)$$

$$\begin{aligned} J_{11} = J_{22} = J_{12} = J &= \frac{1}{2}(\gamma_{aa} + \gamma_{ab}), \\ K_{12} = K &= \frac{1}{2}(\gamma_{aa} - \gamma_{ab}). \end{aligned} \quad (5.10)$$

$$\begin{vmatrix} -W & K & 0 & 0 \\ K & -W-4\beta & 0 & 0 \\ 0 & 0 & -W-2\beta+K & 0 \\ 0 & 0 & 0 & -W-2\beta-K \end{vmatrix} = 0 \quad (5.11)$$

(roots W_N, W_Z, W_V, W_T)

$$W = E - E_1 \quad (5.12)$$

Numerical calculations with these equations give the results in Table III. These show the following interesting and encouraging features:

- (1) The calculation with zero differential overlap, but without empirical correction of γ_{aa} , gives results essentially equivalent to those given by the method of Goeppert-Mayer and Sklar.³¹ These are not good.
- (2) The calculation by the full generalized Hückel method gives results in very good agreement with experiment. In particular, the singlet-triplet split comes out well.
- (3) The effect of the atoms-in-molecules correction that has been introduced is a much lowered mixing of Φ_2 with Φ_1 . This means the simple single configuration molecular orbital wave function is better than ordinarily supposed -- the molecular orbital method is vindicated! Enhancement of ionic character would of course be expected from a comparison of 4.4 and 4.5.
- (4) Only the difference of the electronic repulsion integrals γ_{aa} and γ_{ab} enters the calculation of spectroscopic intervals.

The reason for (1) can be seen rather easily in this case.^{32,33} Approximations of the form

$$\gamma_p(1)\gamma_q(1) = \frac{S}{2} [\gamma_p^2(1) + \gamma_q^2(1)] \quad (5.13)$$

reduce all J's in the full Goeppert-Mayer-Sklar calculation to the form of 5.10, and K to the form of 5.10 up to a factor $1-S^2$ in the denominator, which is close to 1. More will be said later about such Mulliken approximations.

Benzene^{19,24,25,34}

Let us now turn directly to benzene, that molecule about which so much has been said. (Historically, butadiene actually came next^{24,25}).

TABLE III. ELECTRONIC ENERGY LEVELS OF ETHYLENE (ev).^a

State ^b	Goeppert-Mayer and Sklar ^c	Zero Differential Overlap ^d	Generalized Huckel ^e	Exptl.
N	0.0	0.0	0.0	0.0
1	1.3	1.1	0.1	-
T	3.1	3.5	5.8	6.4(?)
V	11.5	11.2	7.6	7.6

a. See references 24, 29 and 31.

b. N is the ground state, 1 is the simple MO single configuration description of the ground state, T is the first excited triplet state, and V is the first excited singlet state.

c. Reference 31.

d. Reference 24. Purely theoretical values are given γ_{aa} .

e. Reference 29. Purely theoretical value for γ_{ab} .

Symmetry has a lot to do with this problem if one wants to describe the situation that way. Actually, use of symmetry (group theoretical) arguments will not give any results that would not come out in the wash anyway. In the description given below, group theory is assumed used only in the determination of the original molecular orbitals, and this part of the argument can be found in the texts (e.g., Eyring, Walter and Kimball). The rest follows from the Slater-Condon rules alone.

Table IV, following the equations, gives results.

$$H_{\pi}(1,2,--,6) = \sum_{\mu=1}^6 H_{\text{core}}(\mu) + \frac{1}{2} \sum_{\mu,\nu=1}^{6'} (e^2/r_{\mu\nu}). \quad (5.14)$$

$$\phi_j = \frac{1}{6} \sum_{p=0}^5 \omega^{jp} \chi_p, \quad \omega = \exp(2\pi i/6), \quad j = 0, \pm 1, \pm 2, 3.$$

$$(\phi_j^* = \phi_{-j}) \quad (5.15)$$

$$\begin{aligned} \Phi_N &\equiv N = (\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_{-1}) = (0\bar{0}1\bar{1}-1-\bar{1}) \\ \Phi_{V_{12}} &\equiv V_{12} = \frac{1}{\sqrt{2}} [(0\bar{0}1\bar{2}-1-\bar{1}) + (0\bar{0}2\bar{1}-1-\bar{1})] && T_{12} \text{ with - sign} \\ \Phi_{V_{-1-2}} &\equiv V_{-1-2} = \frac{1}{\sqrt{2}} [(0\bar{0}1\bar{1}-1-\bar{2}) + (0\bar{0}1\bar{1}-2-\bar{1})] && T_{-1-2} \text{ with - sign} \\ V_{1-2} &= \frac{1}{\sqrt{2}} [(0\bar{0}1\bar{2}-1-\bar{1}) + (0\bar{0}2\bar{1}-1-\bar{1})] && T_{1-2} \text{ with - sign} \\ V_{-12} &= \frac{1}{\sqrt{2}} [(0\bar{0}1\bar{1}-1\bar{2}) + (0\bar{0}1\bar{1}+2-\bar{1})] && T_{-12} \text{ with - sign} \\ V_{-1-2} &= V_{12}^*, \quad V_{-12} = V_{1-2}^* \text{ and similarly with triplets} \\ &&& \text{oo degenerate} \end{aligned} \quad (5.16)$$

$$\begin{aligned} V_{12}^+ &= \frac{1}{\sqrt{2}} (V_{12} + V_{-1-2}) && T_{12}^+ \\ V_{12}^- &= \frac{1}{\sqrt{2}} (V_{12} - V_{-1-2}) && T_{12}^- \\ V_{1-2}^+ &= \frac{1}{\sqrt{2}} (V_{1-2} + V_{-12}) && T_{1-2}^+ \\ V_{1-2}^- &= \frac{1}{\sqrt{2}} (V_{1-2} - V_{-12}) && T_{1-2}^- \end{aligned} \quad \begin{array}{l} \text{Similarly} \\ \left. \begin{array}{l} E_1 \text{ Symmetry} \\ B_{1u} \text{ Symmetry} \\ B_{2u} \text{ Symmetry} \end{array} \right\} \end{array} \quad (5.17)$$

$$\begin{aligned}
 I_i &= \frac{1}{6} \sum_p \sum_q \omega^{i(q-p)} \int \chi_p H_{\text{core}} \chi_q dv \\
 &= \alpha + \frac{1}{6} \sum_p \sum_{q \neq p} \omega^{i(q-p)} \beta_{pq} \\
 &= \alpha + 2 \cos\left(\frac{2\pi i}{6}\right) \beta
 \end{aligned} \tag{5.18}$$

$$(I_0 = \alpha + 2\beta, I_1 = \alpha + \beta, I_2 = \alpha - \beta, I_3 = \alpha - 2\beta)$$

$$\begin{aligned}
 J_{ij} &= \frac{1}{36} \sum_p \sum_q \sum_r \sum_s \omega^{i(q-p)+j(s-r)} \iint \chi_p(1) \chi_q(1) \left(\frac{e^2}{r_{12}}\right) \chi_r(2) \chi_s(2) \\
 &\quad dv(1)dv(2)
 \end{aligned}$$

$$\begin{aligned}
 &= \frac{1}{36} \sum_p \sum_r \delta_{pr} \\
 &= \frac{1}{6} [\chi_{00} + 2\chi_{01} + \chi_{02} + \chi_{03}] \equiv J
 \end{aligned} \tag{5.19}$$

$$\begin{aligned}
 K_{ij} &= \frac{1}{36} \sum_p \sum_q \sum_r \sum_s \omega^{i(q-p)+j(s-r)} \iint \chi_p(1) \chi_s(1) \left(\frac{e^2}{r_{12}}\right) \chi_r(2) \chi_q(2) dv(1)dv(2) \\
 &= \frac{1}{36} \sum_p \sum_q \omega^{(i-j)(q-p)} \chi_{pq} \\
 &= \frac{1}{6} \left[\chi_{00} + 2 \cos \frac{2\pi(i-j)}{6} \chi_{01} + 2 \cos \frac{4\pi(i-j)}{6} \chi_{02} + \cos \frac{6\pi(i-j)}{6} \chi_{03} \right]
 \end{aligned} \tag{5.20}$$

$$K_{00} \equiv J \text{ (does not appear)}$$

$$\begin{aligned}
 K_{01} &= \frac{1}{6} [\chi_{00} + \chi_{01} - \chi_{02} - \chi_{03}] \\
 K_{02} &= \frac{1}{6} [\chi_{00} - \chi_{01} - \chi_{02} + \chi_{03}] \\
 K_{03} &= \frac{1}{6} [\chi_{00} - 2\chi_{01} + 2\chi_{02} - \chi_{03}]
 \end{aligned}$$

$$W = E - E_N, \quad E_N = 2I_0 + 4I_1 + 15J - 4K_{01} - 2K_{02} \tag{5.21}$$

TABLE IV. ELECTRONIC ENERGY LEVELS OF BENZENE (ev).^a

State	GMS ^b	ZDO ^c	GH-I ^d	GH-II ^e	Exptl. ^f
$1A_{1g}$	0.0	0.0	0.0	0.00	0.00
$1E_{1u}$	9.7	9.9	7.0	6.55	6.76
$1B_{1u}$	7.2	7.3	5.3	5.96	5.96
$1B_{2u}$	5.8	5.9	4.9	4.71	4.71
$3E_{1u}$	4.3	4.5	4.5	4.15	—
$3B_{1u}$	3.0	3.2	4.0	3.59	3.59
$3B_{2u}$	5.6	5.9	4.9	4.71	—

a. See references 19, 24, 25, 34 and 35.

b. The original Goepper-Mayer and Sklar calculation, as corrected in reference 35.

c. Zero differential overlap but theoretical integrals -- reference 24.

d. Reference 25. Full generalized Hückel scheme, with integrals γ_{ab} slightly adjusted downwards.

e. Reference 34. Generalized Hückel scheme, fully empiricized. Values of parameters are: $-\beta = 2.371$, $\gamma_{00} = 10.959$, $\gamma_{01} = 6.895$, $\gamma_{02} = 5.682$ and $\gamma_{03} = 4.978$ ev, the last being a purely theoretical value.

f. Other assignments give unreasonable integral values. See reference 34.

$$\begin{aligned}
 W_{1E_{1u}, 3E_{1u}} &= I_1 - I_0 + K_{01} - K_{03} \pm K_{01} = -2\beta + \frac{1}{6} \gamma_{00} + \frac{2}{3} \gamma_{01} - \frac{2}{3} \gamma_{02} - \frac{1}{6} \gamma_{03} \\
 &= -2\beta - \frac{1}{6} \gamma_{00} + \frac{1}{3} \gamma_{01} - \frac{1}{3} \gamma_{02} + \frac{1}{6} \gamma_{03} \\
 W_{1B_{1u}, 3B_{1u}} &= I_1 - I_0 - K_{02} + K_{03} \pm 2K_{03} = -2\beta + \frac{1}{3} \gamma_{00} - \frac{5}{6} \gamma_{01} + \frac{7}{6} \gamma_{02} - \frac{2}{3} \gamma_{03} \\
 &= -2\beta - \frac{1}{3} \gamma_{00} + \frac{1}{2} \gamma_{01} - \frac{1}{6} \gamma_{02} \\
 W_{1B_{2u}, 3B_{2u}} &= I_1 - I_0 + K_{02} - K_{03} \pm 0 = -2\beta + \frac{1}{6} \gamma_{01} - \frac{1}{2} \gamma_{02} + \frac{1}{3} \gamma_{03}
 \end{aligned} \tag{5.22}$$

(Interactions all zero !)

Again the results are most encouraging. Conclusions may be stated as follows:

- (1) Zero differential overlap brings in no special errors.
- (2) The generalized Hückel method gives good agreement with experiment even before it is "fully empiricized". It thus would seem to have a sound basis.
- (3) As before, only the differences of electronic repulsion integrals enter the calculation. (Note from 5.22 that only π 's enter, and from 5.20 that the K 's depend only on differences.)
- (4) Degeneracy between $1B_{2u}$ and $3B_{2u}$ may be noted.

As we have described it, the benzene calculation merely involves a configuration interaction calculation among states that are degenerate in the Hückel approximation:



This has been termed by Moffitt³⁶ first-order configuration interaction. Configuration interaction over and above this, second-order configuration interaction, can be included, and was included by Parr, Craig and Ross in their Goeppert-Mayer-Sklar calculation on benzene²¹ and by Pariser in his polyacene calculation, to be described below.³⁴ How much configuration interaction to include in a given case (short of the ideal complete amount) is a very difficult question to decide.

Pariser's calculations on the polyacenes³⁴

In some rather complete calculations of the spectra of benzene, naphthalene, ..., pentacene, Pariser has made the following basic assumptions (in addition to those of §4):

TABLE V. Parameter values for benzene (ev).

Parameter	"Theoretical" Value ^a	Value Required for Fit of Benzene Spectrum ^b	Value Used by Pariser for Later Calc. ^c
$-\beta$	2.477	2.371	2.371
χ_{00}	11.08	11.383	10.959
χ_{01}	9.065	7.213	6.895
χ_{02}	5.682	5.788	5.682
χ_{03}	4.978	4.978	4.978

- a. Calculated using Slater orbitals or uniformed-charged sphere approximations to them, except for χ_{00} , for which 4.1 is used. See references 24 and 34.
- b. Reference 25 and Table IV above; χ_{03} is calculated theoretically, all other parameters purely empirically.
- c. Reference 34; χ_{02} and χ_{03} are calculated theoretically, the other three parameters empirically to fit the known B symmetry states of benzene. See Table VI below.

Assumption 1: Simple Hückel molecular orbitals (for which the coefficients are known in analytical form) may be taken as the basis for a configuration interaction calculation.

Assumption 2: The configuration interaction calculation may be limited to mixing the ground configuration built from Hückel orbitals and all "singly excited" configurations (configurations derivable from the ground one by one-electron jumps).

Assumption 3: The penetration integrals P_p of 4.2 are the same for all carbon atoms.

Assumption 4: The integrals γ_{pq} may be computed purely theoretically when atoms p and q are farther apart than neighbors; the integrals γ_{00} , γ_{01} and β may be taken as purely empirical quantities with values chosen to fit the three known B-symmetry benzene levels.

The calculations were performed with an IBM 701; the results are summarized in Table VI.

Before discussing the results, I might say a few words about the assumptions. Assumption 1 is a natural one to make and quite practicable; it requires no further comment. Assumption 2 it would be desirable to do without (in which case "any old molecular orbitals would do") but is made to make the problem tractable. Assumption 3 is a vital one in the sense that it defines an alternant hydrocarbon in this theory^{34,23} (along with the usual starred and unstarred divisibility of the atoms); it should be carefully investigated by someone sometime. Assumption 4 we have already seen (Table V) leads to very reasonable integral values indeed. To call the resultant parameters "purely empirical" hardly does the theory justice, it seems to me; every integral has a value which is in the vicinity of a value that can be obtained by a priori theoretical arguments.

To turn now to the results, they are strikingly good, to say the least. Not given in the table are intensities (f numbers); these come out very well too. And the bond orders in naphthalene come out much better than they did in the old Hückel theory, removing a discrepancy of fairly long standing in experiment (bond length) versus theory in this area.^{34,28,40}




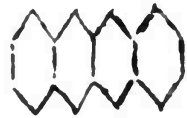

It will be noted that the now experimentally confirmed crossing of the two lowest singlet levels as we go up the series is verified. Even some excited triplets are correctly placed.

Other calculations (by a simpler and by free-electron methods respectively) on polyacenes have been made by Moffitt³⁶ and by Ham and Ruedenberg.³⁸ On naphthalene there are also calculations by Moser³⁷ and Iykos.³⁹

Pariser's calculations on azulene⁴¹

Pariser has applied the same method to azulene, the 5-7 ring analogue of naphthalene. Results again are very good, including this time a computed dipole moment. The same molecule has been treated by Ham and Ruedenberg³⁶ and by Julg.⁴²

TABLE VI. Calculated versus observed excited electronic states of polyacenes (ev).a,b,c

					
Singlets					
B_{2u}^+	6.6	6.3(5.9)	5.3(5.5)	4.7(4.1)	4.1(3.8)
B_{3u}^+	6.6 (6.8)	5.9(5.7)	5.5(5.0)	5.1(4.6)	4.8(4.3)
B_{2u}^-	6.0 (6.0)	4.5(4.5)	3.7(3.4)	3.1(2.9)	2.8(2.4)
B_{3u}^-	4.7 (4.7)	4.0(4.0)	3.7(3.8)	3.6(3.6)	3.5(3.5)
Triplets					
B_{2u}^+	4.2	4.2	3.6	3.2	2.7
B_{3u}^+	4.2 (4.2?)	3.6(3.7)	3.5	3.5	3.5
B_{2u}^-	3.6 (3.6)	2.2(2.5)	1.7(1.7)	1.1(1.2)	0.8
B_{3u}^-	4.7 (4.9?)	4.0	3.7	3.6	3.5

a. Reference 34.

b. Other states than those listed here were considered in reference 34. Also computed were r values, which also came out in good agreement with experiment.

c. Number in parentheses are experimental values. See reference 34 for details.

Butadiene

Butadiene is of course a very important very similar molecule. This has been treated by several people.^{25,44,45}

O₂ and O₂⁺

These molecules also have been treated most successfully.^{32,43} In these molecules χ_0 has been taken as a purely theoretical quantity.

Alternant hydrocarbons

In Table VI degeneracy between singlet and triplet B_{3u}⁻ may be noted. Pariser³⁴ and Pople⁴⁶ have shown that there exists such a degenerate pair for any alternant hydrocarbon. Another theorem of interest is that for an alternant hydrocarbon the charge density is the same on all carbon atoms.^{28,34} Spectra of odd alternant hydrocarbon radicals and ions have been treated by Longuet-Higgins and Pople.⁴⁷

Caution regarding hetero effects

Having seen how successful the theory is for molecules we may think of as "homo" as opposed to "hetero", we might hope that we could proceed confidently to the treatment of some of the latter type, as say methyl-substituted aromatics, or N-heterocyclic analogues of them. We shall see that encouraging results have indeed been obtained for such molecules.

However, a word of caution is in order: this problem is much more difficult than one might first imagine. The trouble is that any such perturbation of a molecule is even with the present simplified theory a many-parameter problem. In general all integrals α_p , β , and χ_{pq} will be affected, even if the number of electrons is not changed. ^{pq}And if the number of electrons is changed (or the number of atoms) new integrals will enter.

It may be that a particular case can be treated satisfactorily treating the number of electrons as constant; we then say that the effects of the perturbation are inductive.²⁹ An example would be the pyridine molecule treated as a six-electron problem. If the number of electrons must be changed, the effects may be called mesomeric. Hyperconjugation in methyl-substituted benzenes would be an example.

To illustrate the problems involved in the general case, there are given below the equations for two-electron ethylene-like molecules.²⁹ It will be noted how what may be termed electronegativities enter. This provides a good check on our theory: it gives the Mulliken formula for the electronegativity of Pauling. It also shows the complexities, though. Not only must electronegativities be handled, but so must effects on the integrals β_{ab} and χ_{ab} , which are hard to assess quantitatively.

χ_a and χ_b not equivalent

$$\phi_1 = \frac{1}{2} (\chi_a + \chi_b), \quad \text{nevertheless} \quad (5.23)$$

$$\phi_2 = \frac{1}{2} (\chi_a - \chi_b).$$

$$\begin{aligned} \Phi_1 &= (\phi_1 \bar{\phi}_1), \quad \Phi_2 = (\phi_2 \bar{\phi}_2), \quad \Phi_V = \frac{1}{\sqrt{2}} [(\phi_1 \bar{\phi}_2) + (\phi_2 \bar{\phi}_1)], \\ \Phi_T &= \frac{1}{\sqrt{2}} [(\phi_1 \bar{\phi}_2) - (\phi_2 \bar{\phi}_1)]. \end{aligned} \quad (5.24)$$

$$H_{11} = 2I_1 + J = \alpha_a + \alpha_b + 2\beta + J,$$

$$H_{22} = 2I_2 + J = \alpha_a + \alpha_b - 2\beta + J,$$

$$H_{VV} = I_1 + I_2 + J + K = \alpha_a + \alpha_b + J + K, \quad (\text{all as before}) \quad (5.25)$$

$$H_{TT} = I_1 + I_2 + J - K = \alpha_a + \alpha_b + J - K,$$

$$H_{12} = K.$$

$$H_{1V} = H_{2V} = \sqrt{2} [I_{12} + (11|12)] . \quad (\text{the new feature}) \quad (5.26)$$

$$I_{12} = \frac{1}{2} (\alpha_a - \alpha_b), \quad (11|12) = \frac{1}{4} (\gamma_{aa} - \gamma_{bb}).$$

But, using 4.1 and 4.3,

$$\alpha_a = - (I_a + \gamma_{ab} + P_a), \quad \gamma_{aa} = I_a - A_a, \quad (5.27)$$

$$\alpha_b = - (I_b + \gamma_{ab} + P_b), \quad \gamma_{bb} = I_b - A_b.$$

Thus

$$H_{1V} = H_{2V} = -2 \frac{1}{2} Y \quad (5.28)$$

where

$$Y = y_a - y_b \quad (5.29)$$

is an electronegativity difference, and

$$\begin{aligned} y_a &= \frac{I_a + A_a}{2} + P_a, \\ y_b &= \frac{I_b + A_b}{2} + P_b, \end{aligned} \quad (5.30)$$

are effective atomic electronegativities. The secular equation for the singlet

states and the corresponding transition moment matrix are as follows:

$$\begin{vmatrix} -W & K & -2^{-1/2}Y \\ K & -W-4\beta & -2^{-1/2}Y \\ -2^{-1/2}Y & -2^{-1/2}Y & -W-2\beta+K \end{vmatrix} = 0 \quad (5.31)$$

$$\begin{pmatrix} M_{11} & M_{12} & M_{1V} \\ M_{21} & M_{22} & M_{2V} \\ M_{V1} & M_{V2} & M_{VV} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 2^{-1/2}eR \\ 0 & 0 & 2^{-1/2}eR \\ 2^{-1/2}eR & 2^{-1/2}eR & 0 \end{pmatrix}. \quad (5.32)$$

These give for the dipole moment of the ground state

$$\begin{aligned} \mu &\approx 2^{1/2}A_{NV}eR \approx 2^{1/2}eR 2^{-1/2}Y / E_V - E_N \\ &= Y[(eR)/(E_V - E_N)] \end{aligned} \quad (5.33)$$

This shows that the electronegativity difference Y enters the dipole moment in the expected way.

N-heterocyclic compounds

With these facts in mind, we should perhaps not be too surprised, even though we may be disappointed, that there has not yet been very much work with heterocyclic substances!

The N-heterocyclic analogues of benzene, pyridine, the isomeric diazines and triazine, were treated successfully in the second of the original papers on the method,²⁵ although for various reasons the work needs redoing. Only pi-pi spectra were considered, but the relative positions and intensities came out fine, including the relative behaviors of the isomeric diazines.

Table VII shows this problem set up in a more elegant way than was originally used.⁴⁸ There is given the secular equation (for singlets) for the arbitrary benzene-like molecule, that is, any six-electron system that can be thought of as a mild perturbation of benzene. You will observe that what is done is to use benzene-like molecular orbitals to start and to make up for that by configuration interaction. (Compare the treatment of the two-electron problem above!) The secular equation then takes a very natural form, with off-diagonal elements that all reduce to zero for the full benzene symmetry. This last can be verified from Table VII by use of the fact that an integral I_{ij} is zero for benzene symmetry if $j-i \neq 0$; an integral $L_{\mu\nu}$ is zero unless $\mu + \nu = 0$. The type of $L_{\mu\nu}$ for which $\mu + \nu = 0$ is one of the usual J's or K's for the problem; the latter notation has been used in the Table so that any L remaining vanishes for benzene symmetry.

The complexity of the effects of a given perturbation is evident. There are "non-vectorial" effects which do not depend on where the perturbation occurs (effects on I_i , J and K_{ij}); there are "vectorial" effects which are position dependent (effects on L_{ij} and I_{ij}). It will be seen that even the diagonal elements may have both kinds of effects in them; the lowest singlet, B_{2u} level is an especially simple case in that "vector" effects do not enter the diagonal element in that case.

This argument can be considerably extended in a useful systematic fashion.⁴⁸

Other calculations of spectra of N-heterocyclic molecules have been made by Dewar and Paoloni⁴⁹ (melamine) and Paoloni (s-tetrazine).⁵⁰

Other calculations of spectra

Considerable other work with spectra has been reported by Longuet-Higgins, Murrell and McEwen.⁵¹⁻⁵⁷ This work will not be discussed further here; its emphasis has been on inductive and mesomeric effects, effects of bringing two conjugated systems near to each other, and special molecules.

Other workers have varied the applications, from the ferrocene molecule through cyclooctatetraene and polyacetylenes.⁵⁸⁻⁶⁵

§6. THE GENERALIZED HÜCKEL METHOD: APPLICATIONS TO OTHER PROPERTIES

With work on "other" properties it seems to me there lies a great challenge: with luck one should be able to correlate and predict many diverse properties. It was in this respect that the old Hückel method was most disappointing; but with an improved method could we not hope to do better?

In several papers, Pople, Hush and others have treated resonance energies and ionization potentials.^{28,29,65-69} Bond orders and bond lengths also have received considerable attention; in addition to works already quoted there are papers for example by Hall,^{70,71} Pritchard and Summer⁷² R. D. Brown and Pennfold,^{73,74} and Peacock and McWeeny.⁷⁵

While parameters obtained from the theory of one property have from time to time been carried over to another property, there has been only one serious attempt to consider several properties simultaneously, the study made by Lykos of the benzene molecule.³⁹

Lykos considered quite carefully the electronic spectra, resonance energy, ionization potential, electron affinity, and diamagnetic anisotropy of benzene, and showed that it is possible to assign semi-empirical values to the several parameters in a way that will reproduce quite well these several experimental data. In this work Lykos has also relaxed the assumption made by earlier authors that non-neighbor resonance integrals were zero.

Some of the results obtained by Lykos are shown in Table VIII.

TABLE VIII. Quantum-chemical properties of the benzene molecule.^a

Property ^b	1	γ_{00}	Coefficient of ^c			Calculated Result ^d	Observed Result ^d
			γ_{01}	γ_{02}	γ_{03}		
$^1B_{2u}$	-2β	0	1/6	-1/2	1/3	4.91	4.91
$^1B_{1u}$	-2β	1/3	-5/6	7/6	-2/3	6.19	6.19
$^1E_{1u}$	-2β	1/6	2/3	-2/3	-1/6	7.02	7.02
$^3B_{1u}$	-2β	-1/3	1/2	-1/6	0	3.79	3.79
$^3B_{2u}$	-2β	0	1/6	-1/2	1/3	4.91	4.91
$^3E_{1u}$	-2β	-1/6	1/3	-1/3	1/6	4.35	4.35
$E_K - E_N$	-2β	0	-1/6	0	1/6	4.55	3.56
$E^+ - E_N$	$-\beta - \Delta$	-1/2	1/3	0	1/6	$-\Delta - 0.02$	9.52
$E^- - E_N$	$-\beta + \Delta$	1/2	1/3	0	1/6	$\Delta - 0.02 + \gamma_{00}$	0.61 to 1.40
χ_{\perp}^{π}	A	-	-	-	-	34×10^{-6}	54×10^{-6}

a. Reference 39. Later unpublished work by the same author has given slightly different results which will appear in the final published report of his work. An explanation of the anomaly in the diamagnetic anisotropy also has been offered.

b. The first six properties listed are the electronic excitation energies from the ground state N to upper states of the indicated symmetries. $E_K - E_N$ is the vertical resonance energy, $E^+ - E_N$ is the first ionization potential, $E^- - E_N$ is the negative electron affinity, and χ_{\perp}^{π} is the diamagnetic anisotropy.

c. Here $\beta = \beta_{01} - \beta_{03}$ and $\Delta = -I - 6\beta_{02} - P$, where I is the ionization potential of the carbon atom and P is a penetration correction. Also, $A = (2\pi eS/hc)^2(8801)$, where S is an effective area of the benzene ring.

d. All quantities are in ev, except χ_{\perp}^{π} , the units of which are ergs per gauss-mole.

§7. THE GENERALIZED HÜCKEL METHOD: CRITIQUE

What sort of a critique can one give for such a theory? It works, which for some people would be sufficient justification, but this would not suffice for you people here today. Is it fundamentally sound? That is, is it based on laws of physics, and is its arithmetic precision arithmetic?

I think that the answer to the first half of the last question is yes, to the second half strictly no but perhaps approximately yes.

In order to elaborate, we may attempt to analyze several facets in the theory.

In the first place, it has been shown quite rigorously that the pi-electron approximation, so-called, corresponds to a very definitely correct method of procedure when the wave functions for the system may be assumed to satisfy the following conditions. First, they must satisfy the conditions of separability of sigma and pi electrons:76-80

(A) The total wave functions are expressible in the form

$$\Psi = A(\Sigma \Pi) = (\Sigma)(\Pi) \quad (7.1)$$

where Π describes the pi electrons and Σ describes the sigma electrons, each of Π and Σ being antisymmetric with respect to interchange of its electrons.

(B) The functions Σ and Π are well-behaved and normalized.

(C) There is a complete orthonormal set of one-electron wave functions $\sigma_1, \sigma_2, \dots; \pi_1, \pi_2, \dots$ such that Σ can be expanded in terms of Slater determinants built from the σ and Π can be expanded in terms of Slater determinants built from the π . And secondly, in addition, the function Σ must be the same for all the molecular states of interest.

If one is willing to accept this model (More will be said about "models" below), the operators H_{core} are well-defined, and it is all right to use the variational principle to determine best pi-electron functions in the manner we have employed. The operator H_{core} of course depends upon the precise form of Σ ; whether we know the latter is immaterial for the justification of our method.

Indeed, as McWeeny first pointed out,^{78,79} this very ignorance of the form of Σ is justification for another feature to the method, the use of empirical core integrals, especially β_{core} . An empirical value may for very fundamental reasons be better than a theoretical one, since we could never be sure we had the right form of Σ in a purely theoretical calculation.

The zero differential overlap matter is more a matter of the arithmetic. This has been considered by several authors, although a complete discussion has not yet been given by anyone. McWeeny's comments seem most clear to me;⁸¹ but Hall's,⁸² Löwdin's,⁸³ and Mulliken's,³³ remarks also may be of help, and those of

Fumi and Parr.³² It just so happens, it appears, that one can essentially duplicate the results of doing a complete calculation with localized orthonormalized atomic orbitals by using the zero differential overlap approximation. Actual calculations by the former method show that exchange and hybrid integrals involving orthogonalized orbitals of this kind are very small indeed and the coulomb integrals have just about the same values as for the non-orthogonalized original orbitals. So that is all there is to it! Löwdin has reservations about the heteropolar case, about which I will say a little more later.

I should also comment on the atoms-in-molecules aspects of this method. As we have seen, Pariser ultimately did quite without atomic data, but the rationalization of his numerical values still lies I think in their direction. Recent work of Arai⁸⁴ should be a useful guide in further study of this question. The fact, that the theory with atoms-in-molecules corrections gives the Mulliken formula for atomic electronegativity,²⁹ seems to me to be a strong indication that Moffitt's basic idea is sound and must be incorporated in any theory of the type that aims to be at all "pictorial" for chemists.

This is not to say that all is finished or all is well. However, in 1954 Moffitt commented:⁸⁵

What is most urgently needed is an approximate, though reliable, method of determining the best molecular orbitals, and of assessing configurational interaction quantitatively for relatively large systems. And it appears that this must stem from the fundamental equations of the method of atoms in molecules rather than from those of antisymmetrized molecular orbital theory. A set of simplifications must be chosen judiciously so as to render these equations more tractable -- and in this connection the work of Pople may provide valuable clues. The work of Pariser and Parr is an important step in this direction. It grafts certain features of Kimball's hard sphere approximation onto the conventional ASMO formalism. The solution of problems is thereby greatly facilitated. Unfortunately it was found necessary to replace some terms by semi-empirical parameters, and this serves to obscure somewhat the underlying basis of their approach.

And in 1956, in speaking of these same matters, McWeeny says:

The simple theory appears to be better founded, in a heuristic sense, than when first advanced.

So at least we seem to me moving in the right direction!

88. THE THEORY OF SEPARATED ELECTRON PAIRS⁸⁷

The above quoted "separability theorem" for sigma and pi electrons was a lot of fun to prove, and it led us to more general considerations with other quite different applications. Here I shall restrict myself to discussion of one other special case,⁸⁷ but it will perhaps be clear how the generalization can be made.⁸⁶ A similar discussion has been given by Hurely, Lennard-Jones and

88 Pople. Those authors however apparently did not have actual calculations in mind, while we shall definitely be concerned with numerical calculations.

The following three conditions may be taken as defining a case of separated electron pairs:

(A) The total wave function Λ has the form

$$\Lambda = ((\Lambda_A)(\Lambda_B)\dots(\Lambda_M)) = [\Lambda_A \Lambda_B \dots], \quad (8.1)$$

where (Λ_A) is an antisymmetric two-electron wave function describing pair A, (Λ_B) an antisymmetric function describing pair B, and so on, and Λ is completely antisymmetric; the parentheses here thus indicate appropriate normalized antisymmetrization operators.

(B) Each of the Λ_I is normalized:

$$\iint \Lambda_I^*(1,2) \Lambda_I(1,2) d\tau_1 d\tau_2 = 1. \quad (8.2)$$

(C) There is some complete orthonormal set of spinorbitals $\lambda_{a1}, \lambda_{a2}, \dots; \lambda_{b1}, \lambda_{b2}, \dots; \lambda_{c1}, \lambda_{c2}, \dots; \dots$ such that Λ_A can be expressed linearly in terms of Slater determinants built from the λ_a , Λ_B can be expressed in terms of determinants built from the λ_b , and so on.

As a consequence of these conditions one has a number of results. The total wave function Λ is normalized. Also, certain orthogonality conditions are satisfied:

$$\int \Lambda_I^*(1,2) \Lambda_J(1,4) d\tau_1 = 0 \text{ for } I \neq J, \quad (8.3)$$

$$\iint \Lambda_I^*(1,2) \Lambda_J(1,2) d\tau_1 d\tau_2 = 0 \text{ for } I \neq J. \quad (8.4)$$

(These two equations at first sight seem equivalent, but they are not; the second follows from the first but the first does not follow from the second. Indeed, it would be of considerable interest to develop the whole theory for the case for which 8.4 holds but not 8.3. We could then say we have almost separated electron pairs, and even talk of "almost separabilities of various orders, depending on how many spinorbitals two pair descriptions have in common -- see Condition C above.)

Making definitions as indicated, one can derive the following formulas for a case of separated electron pairs. Note that E here is the electronic energy; to get the total energy one must add the nuclear repulsion energy

$$H_{el}(1,2,\dots,2n) = \sum_{\zeta=1}^{2n} H_N(\zeta) + (1/2) \sum_{\zeta, \eta=1}^{2n} (e^2/r_{\zeta\eta}) \quad (8.5)$$

$$H_N(\zeta) = U_N(\zeta) + T(\zeta) \quad (8.6)$$

$$E_{\Lambda}^{el} = \sum_I I_I + (1/2) \sum_I \sum'_{J \neq I} (J_{IJ} - K_{IJ}) \quad (\text{additive partition}) \quad (8.7)$$

$$= \sum_I E_I - (1/2) \sum_I \sum'_{J \neq I} (J_{IJ} - K_{IJ}) \quad (\text{subtractive partition}) \quad (8.8)$$

$$= \sum_I \bar{E}_I \quad (\text{median partition}) \quad (8.9)$$

$$E_I = I_I + \sum_{J \neq I} (J_{IJ} - K_{IJ}) \quad (8.10)$$

$$\bar{E}_I = (1/2) (E_I + I_I) \quad (8.11)$$

$$J_{IJ} = 4 \int \Lambda_I^*(1,2) \Lambda_J^*(3,4) (e^2/r_{13}) \Lambda_I(1,2) \Lambda_J(3,4) d\tau_1 d\tau_2 d\tau_3 d\tau_4 \quad (8.12)$$

$$K_{IJ} = 4 \int \Lambda_I^*(1,2) \Lambda_J^*(3,4) (e^2/r_{13}) \Lambda_I(3,2) \Lambda_J(1,4) d\tau_1 d\tau_2 d\tau_3 d\tau_4 \quad (8.13)$$

$$I_I = \int \Lambda_I^*(1,2) H^0(1,2) \Lambda_I(1,2) d\tau_1 d\tau_2 \quad (8.14)$$

$$H^0(1,2) = H_N(1) + H_N(2) + (e^2/r_{12}) \quad (8.15)$$

These equations are of a familiar form; the J_{IJ} are generalized coulomb integrals, the K_{IJ} are generalized exchange integrals, and the I_I are generalized core integrals -- I_I is the energy pair I would have in the state Λ_I if the other pairs were absent.

It is important that one does not have equality between self-coulomb and self-exchange integrals in this case, that is

$$J_{II} \neq K_{II}. \quad (8.16)$$

This means that if one attempts to write out a generalized Hartree-Fock set of equations one will get stuck at the stage when one wants to make the self-consistent operator the same for all pair functions. One cannot replace the primed summations in 8.7 and 8.8 by unprimed summations.

Another self-consistent procedure seem better. To get this, we recast the energy in still another form, to focus attention let us say on pair K :

$$E_{\Lambda}^{el} = E_{\Lambda-K}^0 + E_K \quad (8.17)$$

$$E_{\Lambda-K}^0 = \sum_{I \neq K} I_I + (1/2) \sum_{I \neq K} \sum_{J \neq K, I} (J_{IJ} - K_{IJ}) \quad (8.18)$$

This quantity $E_{\Lambda-K}^0$, you will note, is independent of Λ_K . Further, the pair K energy E_K can be written in the following form:

$$E_K = \iint \Lambda_K^*(1,2) H_K(1,2) \Lambda_K(1,2) d\tau_1 d\tau_2 \quad (8.19)$$

$$H_K(1,2) = H^0(1,2) + G_{\Lambda-K}(1,2) + (e^2/r_{12}) \quad (8.20)$$

$$= H_{\Lambda-K}(1) + H_{\Lambda-K}(2) + (e^2/r_{12}) \quad (8.21)$$

$$H_{\Lambda-K}(1) = H_N(1) + G_{\Lambda-K}(1) \quad (8.22)$$

$$G_{\Lambda-K}(1) = J_{\Lambda-K}(1) - K_{\Lambda-K}(1) = \sum_{I \neq K} G_I(1) \quad (8.23)$$

$$J_{\Lambda-K}(1) = \sum_{I \neq K} J_I(1) \quad , \quad K_{\Lambda-K}(1) = \sum_{I \neq K} K_I(1) \quad (8.24)$$

$$J_I(1)\phi(1) = \iint \Lambda_I^*(3,4) [(e^2/r_{13}) + (e^2/r_{14})] \Lambda_I(3,4)\phi(1) d\tau_3 d\tau_4 \quad (8.25)$$

$$K_I(1)\phi(1) = \iint \Lambda_I^*(3,4) [(e^2/r_{13}) \Lambda_I(1,4)\phi(3) + (e^2/r_{14}) \Lambda_I(3,1)\phi(4)] d\tau_3 d\tau_4 \quad (8.26)$$

Thus we have a perfectly well-defined operator $H_K(1,2)$ describing the problem of determining the pair K function; if we choose to assume the rest of the molecule fixed, we can apply the variation method quite legitimately to this two-electron problem. Or, we can iterate: assumed all but pair K fixed, adjust pair K; take this and all of the rest of the pairs but one, say L, fixed and adjust pair L, and so on, until the best separated electron pair description of the given system is obtained. We have successfully used this method in numerical calculations,⁶⁵ as will be described in the next section.

In carrying out such a determination of a total wave function Λ we must be careful not to violate the separability conditions A, B and C. In practice we ordinarily assume this by fixing the basic set of functions and their partitioning.

To illustrate all of this and to anticipate a little the actual calculations to be reported in the next section, I shall now indicate how we proceed to find the best orbital description of a system of separated electron pair bonds. By this we mean the best description such that the bond I function is describable in terms of the two atomic orbitals χ_{IA} and χ_{IB} , with the orbitals for separate pairs orthogonal. Restricting the discussion to the case of all singlet functions we thus have for bond K, say, the variation function

$$\Lambda_K = A_{K1} \Phi_{K1} + A_{K2} \Phi_{K2} + A_{K3} \Phi_{K3} \quad (8.27)$$

where (compare §5)

$$\bar{I}_{K_1} = (\phi_{K_1} \bar{\phi}_{K_1}), \bar{I}_{K_2} = \frac{1}{\sqrt{2}} [(\phi_{K_1} \bar{\phi}_{K_2}) + (\phi_{K_2} \bar{\phi}_{K_1})], \bar{I}_{K_3} = (\phi_{K_2} \bar{\phi}_{K_2}) \quad (8.28)$$

with

$$\phi_{K_1} = \frac{1}{\sqrt{2(1+S)}} (\chi_{Ka} + \chi_{Kb}), \phi_{K_2} = \frac{1}{\sqrt{2(1-S)}} (\chi_{Ka} - \chi_{Kb}) \quad (8.29)$$

The Hamiltonian operator has the form of 8.20 to 8.26 in which we can show now, by straightforward application of Slater-Condon rules, that

$$G_I = (A_{I_1}^2 + \frac{1}{2}A_{I_2}^2)(2J_{11} - K_{11}) + (A_{I_3}^2 + \frac{1}{2}A_{I_2}^2)(2J_{22} - K_{22}) + \sqrt{2} A_{I_2}(A_{I_1} + A_{I_3})(2J_{12} - K_{12}) \quad (8.30)$$

in which the one-electron coulomb and exchange operators are defined by equations as follows:

$$J_{\lambda\lambda'}(1)\phi(1) = \int \lambda^*(2)\lambda'(2)(e^2/r_{12})\phi(1)d\tau_2 \quad (8.31)$$

$$K_{\lambda\lambda'}(1)\phi(1) = \int \lambda^*(2)\phi(2)(e^2/r_{12})\lambda'(1)d\tau_2 \quad (8.32)$$

(In 8.30, instead of writing full indices, we have written only the index labeling the molecular orbital.) This equation for G_I you will note is "spin-free" (which the general G_I of 8.23 is not) and exact within the stated defining characteristics of the model. It could be used in purely theoretical calculations in complicated cases.

However, our interest we can characterize as "semi-theoretical" at the moment; we would like to explore approximate treatments of these equations in the first run, so to speak. To this end, let us immediately make the simplifying Mulliken approximation

$$2J_{ab} = S_{ab}(J_{aa} + J_{bb}) \quad (8.33)$$

and the generalized Mulliken approximation (for use only in calculation of inter-bond effects)

$$2G_{ab} = S_{ab}(G_{aa} + G_{bb}), \quad (8.34)$$

where the operators now are defined over atomic orbitals (subscripts K or I suppressed). Then the above 8.30 simplifies all the way to the very convenient form

$$G_I = (G_{aa} + G_{bb}) + Q_I(G_{aa} - G_{bb}) \quad (8.35)$$

where

$$Q_I = \frac{\sqrt{2}}{\sqrt{1-S}} A_{I_2}(A_{I_1} + A_{I_3}) \quad (8.36)$$

This will be of basic importance in our subsequent discussion.

Returning now to the linear variational problem of determining the best pair K function of the form 8.27, using 8.33 and 8.34 the matrix elements for the problem reduce to the following forms: (superscripts or subscripts K suppressed)

$$\begin{aligned} H_{11} &= \alpha_a + \alpha_b + 2(1-S)\beta + \frac{1}{4}(\gamma_{aa} + \gamma_{bb} + 2\gamma_{ab}) \\ H_{22} - H_{11} &= -2\beta + \frac{1}{4}(1-S^2)^{-\frac{1}{2}}(\gamma_{aa} + \gamma_{bb} - 2\gamma_{ab}) \\ H_{33} - H_{11} &= -4\beta \\ H_{12} = H_{23} &= [2(1-S^2)]^{-\frac{1}{2}}[(\alpha_a - \alpha_b) + \frac{1}{2}(\gamma_{aa} - \gamma_{bb})] \\ H_{13} &= \frac{1}{4}(1-S^2)^{-\frac{1}{2}}(\gamma_{aa} + \gamma_{bb} - 2\gamma_{ab}) \end{aligned} \quad (8.37)$$

Here the γ 's are the previously defined electronic repulsion integrals over the pair K orbitals; the α 's and β are core integrals involving $H_{\Lambda-K}$, viz:

$$\alpha_a \equiv \alpha_{Ka} = \int \chi_{Ka}^*(1) H_{\Lambda-K}(1) \chi_{Ka}(1) dv(1) \quad (8.38)$$

$$\begin{aligned} &= \alpha_{NKa} + \sum_{I \neq K} [(\int \chi_{KaIa} + \int \chi_{KaIb}) + Q_I(\int \chi_{KaIa} - \int \chi_{KaIb})] \\ \alpha_b &= \alpha_{NKb} + \sum_{I \neq K} [(\int \chi_{KbIa} + \int \chi_{KbIb}) + Q_I(\int \chi_{KbIa} - \int \chi_{KbIb})] \end{aligned} \quad (8.39)$$

$$\begin{aligned} \alpha_{NKa} &= \int \chi_{Ka}^*(1) H_N(1) \chi_{Ka}(1) dv(1) \\ &(\alpha_{NKb} \text{ similarly}) \end{aligned} \quad (8.40)$$

$$\begin{aligned} \beta = \beta_K = \beta_{NK} &= \frac{1}{2} (1-S^2)^{-\frac{1}{2}} \left[\int \chi_{Ka}^*(1) H_N(1) \chi_{Kb}(1) dv(1) + \int \chi_{Kb}^*(1) H_N(1) \chi_{Ka}(1) dv(1) \right. \\ &\quad \left. - S(\alpha_{NKa} + \alpha_{NKb}) \right] \end{aligned} \quad (8.41)$$

$$\int_{pq} \equiv (pp|qq) - \frac{1}{2}(pq|pq) \quad (8.42)$$

The equation 8.41 is especially interesting; it shows that the quantity β is independent of the presence of and the polarity of the other bonds than bond K -- it is very insensitive to its environment.

One now needs only numerical values in order to solve the secular problem for pair K, and one can then iterate for the other pairs.

Certain implications can now be noted regarding electronegativity. Recalling our previous argument that the electronegativity difference is essentially H_{12} and looking at 8.39, we see that now some new terms enter which bring in the effects of the other bond polarities. In fact, one finds, in place of the previous 5.30, the result:

$$y_{Ka} = \frac{1}{2} (I_{Ka} + A_{Ka}) + P_{Ka} + \sum_{I \neq K} Q_I (\sum I_{aKa} - \sum I_{bKa}), \quad (8.43)$$

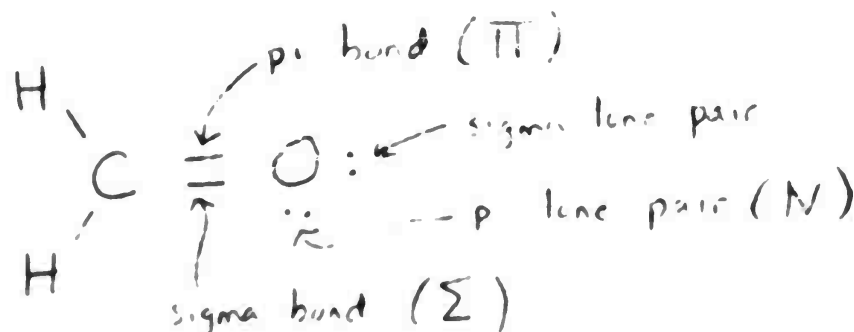
and similarly for y_{Kb} . Since the pair K moment comes out essentially proportional to $y_a - y_b$, we see that the pair I moments enter in the pair K moments linearly with coefficients which are electronic repulsion integrals. This may be thought of as a quantitative evaluation of dipole-dipole inductive effects between bonds.

It is interesting to carry the analysis of total energy further, adding to the electronic energy in the form 8.9 the nuclear-nuclear repulsion energy. This can be done in a way which makes the total energy a sum of individual bond energies. Furthermore, under certain natural assumptions the individual bond energies turn out to be environment-independent, as we would expect.⁸⁷

§9. SIGMA-PI INTERACTION EFFECTS IN THE FORMALDEHYDE MOLECULE

Parks⁶⁵ has carried out some extensive calculations on the formaldehyde molecule which well illustrate what can be done with the sort of techniques I have just described.

The conventional description of this molecule, as sketched, involves an assumed "separability" of the various electron pairs. What Parks has done is to put such a description into precise quantum-mechanical terms, and to test it numerically.



Details of Parks' work I will not give here. What he did was to assume a fixed "core" in the field of which the pi-electrons, the sigma electrons in the CO bond and the pi lone pair electrons move, described respectively by anti-symmetric wave functions Π , Σ , N and collectively by totally antisymmetric wave functions of the type $(\Pi \Sigma N)$. If the wave functions Π are built from pi AO's $2p\pi_C$ and $2p\pi_O$, the wave functions Σ from Sigma AO's $2p\sigma_C$ (an sp^2 hybrid) and $2p\sigma_O$ (pure p), and the wave functions N from a pi AO $2p\pi_O$, appropriate conditions of separability are satisfied so that one pair at a time may be treated, in the manner I have described above. Various integrals over the basic orbitals are

needed, as are various properties of the "core" assumed for the problem. But once these are known a best wave function of the type ($\sum I I N$) can be constructed for each of several molecular states of interest, and the effects of reorganization in one part of electronic excitation or ionization in another part can be assessed.

The several integrals are not known a priori, so one must proceed in part semi-empirically. This is what Parks did. The most important integrals he employed in one of his calculations are given in Table IX, with an indication of how he obtained them; results for various molecular properties and reorganization effects are given in Table X.

The actual manner in which Parks carried out these calculations was of necessity complicated -- it is easier to write out the various properties in terms of the basic integrals than to determine the integrals from the properties, which he had to do! But once the work has been done, the parameters may be used as basis for calculations on other molecules. And I myself consider it quite important to test very fully the possibility of semi-quantitative calculations at the level of complexity represented by the chemists' qualitative orbital notions.

The reorganization effects, you will observe, are quite small.

TABLE IX. Formaldehyde: basic integrals (Calculations 3).^{a,b}

Integral	Source
One-center electronic repulsions	
-11.42 ev	Obtained from atomic spectroscopic data -- Slater-Condon treatment
-14.68	
10.842	
11.217	
10.164	
1.231	
-17.32	
-15.06	
-14.671	
12.865	
0.903	
Two-center electronic repulsions	
8.6356	Obtained by systematic slight downward adjustment of purely theoretical values calculated for Slater orbitals
12.8317	
8.2782	
9.8658	
8.6348	
0.129	
0.109	
0.038	
Core integrals	
-53.1147	Obtained by empirical fitting of six experimental data as indicated in Table X
-70.4262	
-3.0214	
-62.625	
-71.7238	
-3.252	

^aFor details, see reference 65.

^b"Calculation 3" is only one of several calculations carried out in reference 65.

TABLE X. Formaldehyde: results (Calculation 3).^a

State ^b	Q_{π}^c	Q_{σ}^c	Energy (ev) ^d
Ω_N	-0.297	0.049	0.00($\mu = 2.34D$)*
$3\hat{L}(n \rightarrow \pi^*)$	-0.330	0.049	4.24
	-0.264	-0.308	3.90(3.02)
$1\hat{L}(n \rightarrow \pi^*)$	-0.386	0.049	4.55
	-0.350	-0.258	4.23(4.26)*
$1\hat{L}(n \rightarrow \sigma^*)$	-0.297	-0.160	7.15
	-0.362	-0.154	7.10(7.10)*
$\hat{L}(\pi \rightarrow \pi^*)$	-0.436	0.049	8.03
	-4.72	0.172	8.00(8.00)*
$2\hat{L}(n^+)$	-0.566	0.049	11.11
	-0.521	-0.274	10.83(10.82)*
$2\hat{L}(\pi^+)$	-0.342	0.049	12.20
	-0.328	-0.042	12.18
$2\hat{L}(\sigma^+)$	-0.297	-0.262	13.23
	-0.441	-0.095	13.10(13.10)*

- a. The first and second rows in each case give the results before and after reorganization of the rest of the electrons to the indicated excitation or ionization.
- b. In order these states are: ground state, triplet state arising from excitation of a lone pair electron to an anti-bonding pi orbital in the CO bond, singlet state arising from the same excitation, singlet state arising from excitation of a lone pair electron to an anti-bonding sigma orbital in the CO bond, singlet state from excitation of a pi electron from a bonding to an anti-bonding orbital in the CO bond, and ionized states resulting from ionization of a lone pair electron, a pi electron in the CO bond, and a sigma electron in the CO bond.
- c. Negative unit Q means one unit e of negative charge on the oxygen atom; Q_{π} gives the distribution of charge in the pi part of the CO bond, Q_{σ} that in the sigma part.
- d. * indicates data used for calibration. Experimental values are in parentheses.

§ X. CONCLUSIONS: THE PRESENT STATUS AND FUTURE DEVELOPMENT
OF THE QUANTUM THEORY OF VALENCE

My point of view on how research should be prosecuted in the quantum theory of valence by now should be amply evident -- in brief, I advocate a many-sided attack. Nevertheless it may be of interest to give a more detailed breakdown of my general philosophy, which I shall try to do now.

Some general principles

Concerning purely theoretical calculations:

- (1) These cannot and should not be denied; they will serve more and more as the guide for all workers in the field.
- (2) As purely theoretical methods develop, new methods will be developed for their interpretation.
- (3) The electronic computer is indispensable.

Concerning semi-empirical calculations:

- (4) These cannot and should not be denied; for complicated molecules they will always be the way.
- (5) These should be patterned after the purely theoretical methods but with the simple theories of the chemist as a guide too. One is seeking precise ways of getting approximate results of estimable error.
- (6) These should be made usable for more and more people; there is no place for elegance for elegance's sake.
- (7) The electronic computer is indispensable.

General:

- (8) Optimism should prevail. One should accentuate the positive, and cynics should go elsewhere.
- (9) The problem of molecular properties is a problem of numbers, not of words. So beware of arguments which transform equations without solving them.
- (10) One should be patient; all of the consequences of Newton's laws were not obtained in a matter of decades! (A remark made by Professor Mulliken to me a few years ago.)

Some working rules

In purely theoretical calculations:

- (1) One should treat more and more cases with very accurate methods (to remove all ambiguities and all doubts).
- (2) One should treat various simplified models accurately (to establish reasonable approximate methods).

(3) One should be on the lookout for new basic functions (to improve the convergence and ease of calculations).

(4) One should work to make the calculations more and more fully automatic (to free the chemists and physicists for the jobs of basic interpretation and application).

In the semi-empirical calculations:

(5) One should keep a close watch on purely-theoretical developments (to enable one to incorporate their most essential features at each stage).

(6) One should carry out both semi-empirical calculations and purely-theoretical calculations where possible on the same molecules or molecular properties (to get a true test of the validity of the semi-empirical methods).

(7) One should try to incorporate in some proper way into molecular theories the vast data of atomic spectra and other properties (to explore fully this ramification of the old chemists' notion that the properties of molecules can be described in terms of the properties of atoms).

(8) One should try to translate the best of the organic chemists' notions into quantum-mechanical equations (to properly put such notions to quantitative test).

(9) One should try to incorporate more and more properties in semi-empirical theories, for more and more molecules.

(10) One should remain on the lookout for ways to simplify the mathematics (to make problems tractable).

Illustrations

I would argue that the most important papers in the current literature obey the above "rules".

The papers of Boys beautifully illustrate rules (1) and (4),³ and he has stated very clearly the case for the electronic computer.

Rule (2) represents just what everyone has been doing for years. There is a healthy new emphasis rightly coming here, however, on the frank stating of all postulates, in precise quantum-mechanical terms for all to see.

Rule (3) does not guarantee progress -- one must depend on the stochastic method! A recent promising paper of Harris provides a good example.⁸⁹

No comment is required on Rules (5) and (6), which are self-evident.

Rule (7) was of course the impetus for Moffitt's important work.^{22,23} But this in my opinion was only a beginning: Arai and Hurley have carried the argument further in very recent papers.^{84,90-92}

To illustrate (8) one could point to papers such as those of Taft as providing the challenge.⁹³ And as for (9), you all know how much information in need of interpretation is being accumulated through nuclear and electronic resonance spectroscopy.

Finally, let me elaborate a little on Rule (10) and what it means to me. There are many examples of where clever persons have made clever approximations to make a particular calculation tractable, and such devices are and will remain useful. But there is a greater hope which we, as optimists, may have. Schrödinger's mechanics would serve our purposes exactly, but we find it difficult to carry through the mathematics. To obtain the accuracy we need, which is not the ultimate, why do we not seek another, more workable, a "pseudo-classical", postulatory basis?

Thank you very much, and good luck!

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